

Organotin Compounds and Their Use for Insect and Mite Control

by R. C. Hunter*

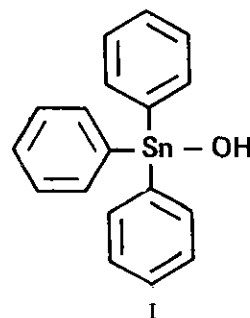
A brief overview of biological activity of organotin compounds is given, with emphasis on activity against plant-feeding arthropods. Plictran miticide, containing cyhexatin (tricyclohexylhydroxystannane), the first product to be fully commercialized for control of plant-feeding mites on a broad range of agricultural crops, is used as a model to indicate the chemistry and potential performance, phytotoxicity, residues, limitations on usage, environmental acceptability, and use patterns for products containing similar organotin compounds.

Published reviews of the biological activity of organotin compounds point out that the broad spectrum of toxicity of heavy metals as well as organometallic compounds has been recognized for a long time but that, unlike a number of other metals, tin and its inorganic compounds possess no noteworthy fungicidal or other biologically interesting properties. Nevertheless, in the early 1950's unexpected fungicidal and biocidal agents were found among the organic compounds of tetravalent tin. Subsequently it has been determined that tin compounds of this type have many potential uses.

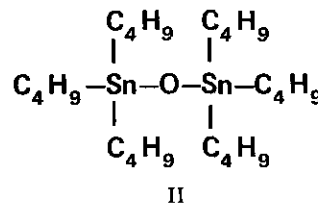
The triaryltins have been shown to have activity as antifoulants, bactericides, molluscides, algicides, anthelmintics, fungicides, insect antifeedants, acaricides, chemosterilants, and insecticides. Because of their relatively low phytotoxicity many of these compounds can be used for plant protection.

One example of such a compound is triphenyltin hydroxide (I) designated by the common name fentin hydroxide and the trade name Du-Ter. The acetate form is designated as fentin acetate and the trade name Brestan. These chemicals have been developed commercially for the control of a number of agriculturally important fungi.

The open-chain trialkyltins, represented by tri-n-butyltin oxide (II), have inherent activity as insecticides, fungicides, and rodent repellants. However,



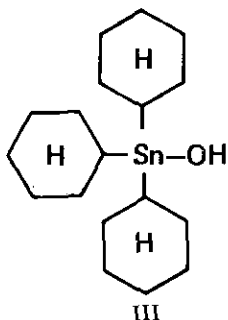
these compounds, even though highly fungitoxic *in vitro*, have not proved to be useful for plant protection. They are generally phytotoxic and essentially ineffective as plant fungicides in greenhouse and field tests, possibly because of their relatively high volatility.



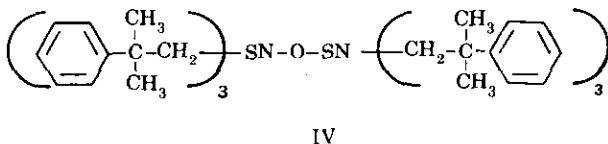
A number of closed-chain trialkyltin compounds have shown biological activity against arthropod pests of plants, particularly as antifeedants and sterilants. Although considerable work has been done with hexamethylditin and others, none have been successfully commercialized for insect control.

*Ag-Organics Department, The Dow Chemical Company, Midland, Michigan 48640.

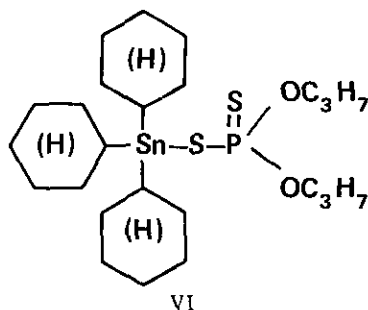
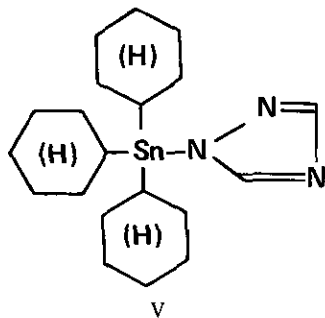
Certain compounds of this type have shown most promise as acaricides. An example is tricyclohexylhydroxystannane (III), designated by the common name cyhexatin and the trade name Plictran. This is the first chemical of this type to be commercially developed on a global basis for the control of plant-feeding mites on a broad range of agricultural crops.



In addition to cyhexatin a number of other organotin compounds are under development as acaricides. The one most advanced toward full commercialization is hexakis(β,β -dimethylphenethyl) distannoxane (IV), manufactured by Shell Chemical and being developed under the trade name Vendex in the U.S. and Torque in certain other countries.



Other compounds in earlier stages of development are Bay Bue 1452, 1-(tricyclohexylstannyl)-1H-1,2,4-triazole, (V), a product of Chemagro, and S-tricyclohexyltin O,O-diisopropylphosphorodithioate (VI) R-28627, a product of Stauffer. Very little information is available on the status of development of these products.



Since Plictran miticide containing tricyclohexylhydroxystannane is in full commercial use and its registered uses fairly well represent those of other organotin compounds, it will be utilized in subsequent discussion to represent this class of chemicals for insect and mite control.

Technical grade (97% purity) cyhexatin is a whitish, nearly odorless powder (Table 1). This compound has no true melting point; it converts to bistricyclohexyltin oxide at 121-135°C and decomposes at 228°C. Vapor pressure is nil at 25°C. It is essentially insoluble in water and solubility in organic solvents is variable but generally low. It is stable in suspensions ranging in pH from slightly acid to alkaline.

The biological activity of cyhexatin can be briefly characterized as follows. It has broad-spectrum activity on motile forms of plant-feeding mites. The current U.S. label lists 12 species that are controlled on various fruit, nut and ornamental plants. It is effective on mite populations resistant to other miticides, including dicofol, dinitros, and organophosphates. In a number of countries it has

Table 1. Chemical and physical properties (97% purity) of cyhexatin (tricyclohexylhydroxystannane).

Property	
Appearance	Whitish powder
Odor	Nearly odorless
Melting point	—
Vapor pressure at 25°C	0
Solubility at 25°C, g/100 ml	
Acetone	0.13
Benzene	1.6
Carbon tetrachloride	2.8
Chloroform	21.6
Methanol	3.7
Stoddard solvent	0.15
Water	<0.0001
Xylene	0.36
Stability	Stable in suspensions from slightly acid to alkaline

become the product of choice for controlling resistant mites on many crops. To date there has been no evidence of development of mite resistance to cyhexatin. It is effective at low rates. On fruit, nut and ornamental plants it is registered for use in the U.S. at rates of 2-3 oz active ingredient/100 gal of spray.

Phytotoxicity of Plictran miticide is generally low, and at recommended use rates and timing it is not injurious to foliage nor does it affect fruit finish. Injury to citrus foliage may occur if it is applied to flush growth and citrus fruit finish may be affected if the product is applied before the fruit has hardened off. Although Plictran miticide is compatible with most of the commonly used orchard pesticides, application of oil in tank mix or separately within 28 days of application of Plictran may cause foliage injury to stone fruits, nuts, and citrus and surface fruit injury to pears and citrus.

Plictran miticide was first registered in 1968 in Chile. It is currently registered in 34 countries for use on a broad variety of crops: tree fruits such as apples, pears, and citrus; small fruits such as raspberries and strawberries; tree nuts such as almonds and walnuts; vegetables such as beans and tomatoes; ornamental shrubs and flowers; and other miscellaneous crops such as tea and hops.

Since cyhexatin is not systemic in plants, residues basically occur on the surface of treated plant tissue. Tolerances have been established on many crops in many countries. To use the U.S. as an example, tolerances have been established on approximately 25 plant and animal tissues. These tolerances range from 0.05 ppm in milk fat to 90 ppm in dried hops.

At the 1970 Joint Meeting of the FAO Working Party of Experts on Pesticide Residues and the WHO Expert Committee on Pesticide Residues, an estimation was made for cyhexatin for a temporary acceptable daily intake of 0.0075 mg cyhexatin/kg of body weight for man. Temporary maximum residue limits have been recommended in apples, pears, citrus fruit, tea, meat, milk, and milk products. Further toxicological and residue work needed for establishment of permanent tolerances was also outlined.

To ensure that residues do not exceed established tolerances, certain limitations for the use of the product have been placed on the product labels. In the U.S., withdrawal periods, i.e., time from last application to harvest, range from none on citrus and stone fruits to 21 days on hops. In other countries the withdrawal periods range from none to 30 days. In some cases, the long withdrawal periods were not imposed due to residue levels but simply by availability of data from normal timing of application for pest control.

Maximum total usage is limited in some cases by limiting the number of applications and in some cases by limiting the total pounds per acre that can be used in one crop season. As examples, only one application per picking stage can be made to tea in Japan and no more than 6 lb/acre per year can be applied to apples in the U.S. As in the case of withdrawal periods, these limitations are sometimes not dictated by the amount of residue that occurs but simply by the data available based on practical usage of the chemical for effective pest control.

Cyhexatin has characteristics which make it environmentally very acceptable. It is essentially nontoxic to insects at acaricidal use rates; thus it has utility in integrated control or pest management programs since it does not destroy many parasitic and predatory insects. The same characteristic makes it nonhazardous to bees which are important pollinators of many crops on which the chemical is used. It does not present undue hazards to fish because it is not applied to bodies of water and does not readily run off into them. Acute toxicity and reproduction tests indicate that at acaricidal use rates the residues in the environment are not hazardous to birds. Acute and chronic feeding studies show that cyhexatin is primarily excreted in the feces and does not accumulate in animal tissues. The compound degrades to inorganic forms of tin and does not accumulate in the environment.

Plictran miticide is generally marketed as wettable powders which are suspended in water and applied as full-cover foliar sprays. The most common application equipment is the speed sprayer or mist blower. There are various modifications but the uniform deposit of the pesticide is generally accomplished by a strong flow of air which breaks up liquid particles from conventional nozzles and carries them to the target surface. One version of this type of equipment is the low-volume speed sprayer which achieves adequate deposit using a much lower gallonage than the standard speed sprayer. Other application equipment includes the hydraulic orchard gun which depends upon high pressure on the spray mixture to achieve particle breakup and deposit on foliage. Equipment such as boom sprayers mounted on conventional or high-clearance tractors are used for row crops. Backpack sprayers are used for application to small areas or to small plants.

Plictran miticide is applied with aerial equipment in some countries and registration is expected for aerial applications on certain crops in the U.S. Research has been conducted with dusts to achieve coverage on certain crops; although performance data are favorable, no registrations for such formulations have been obtained.

Because of the type of formulation, methods of application, and use patterns, the most likely exposure of people to the chemical would be through inhalation and dermal exposure of applicators and dermal exposure of farm workers who enter fields or orchards after applications are made. Adherence to precautionary statements on product labels are adequate to avoid any undue hazards to these people.

Consideration of establishment of re-entry intervals for farm workers has thus far largely been confined to compounds which are cholinesterase inhibitors. Since cyhexatin is not a cholinesterase inhibitor, no re-entry intervals have been proposed.

Available information indicates that the biological activity and use patterns for Vendex are similar to those of Plictran. Very little is known about

other compounds in this group. In summary, by using cyhexatin as a model, a number of generalizations about similar organotin compounds can be made: (1) they are very effective at low rates of application; (2) they are not phytotoxic; (3) they are effective against populations resistant to dicofol, ovex, dinitro compounds, and organophosphate miticides; (4) they are suitable for pest management programs because of specificity on mites; (5) they are safe to applicators and farm workers; (6) they are not hazardous to fish and birds; (7) they are degradable in the environment.

For these reasons, such compounds are highly desirable for controlling plant-feeding mites and appear to have a significant place in agricultural pest control programs throughout the world.